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(54) Title: VINYL CHLORIDE POLYMER/NEOPENTYL GLYCOL BIS (DIPHENYL PHOSPHATE) COMPOSITIONS

(57) Abstract: A vinyl chloride resin composition contains, as the major plasticizer, a neopentyl glycol bis(diphenyl phosphate) composition in an amount that is no less than about 25% by weight, based upon the vinyl chloride resin being present at 100%, by weight.

VINYL CHLORIDE POLYMER/NEOPENTYL GLYCOL BIS(DIPHENYL PHOSPHATE) COMPOSITIONS

Triaryl phosphate esters (for example, tricresyl phosphate) are recognized as one of the earliest primary commercial plasticizers for flexible vinyl chloride resins (hereinafter also referred to as "PVC"). These plasticizers are still used in vinyl composites to aid in conferring flexibility upon such compositions, but their main contribution is in regard to flame retardancy. Careful selection of the appropriate phosphate esters is critical for affecting the desired degree of flame retardancy. Trialkyl phosphates are too volatile for most vinyl applications. Triaryl phosphates are excellent flame retardant plasticizers but may generate too much smoke to pass current building codes and standards (namely, ASTM-E-84, the Steiner Tunnel test). Alkyl diphenyl phosphates, although slightly less effective as flame retardants, have, because of their alkyl side chain, the characteristic of producing less smoke in vinyl formulations since they have a lowers phenolic moiety content, which is well known for generating smoke. In fact, there is sufficient proof that slightly increasing the aliphatic chain length contributes to lower smoke generation.

Often, the effort to improve flame resistance is counterproductive to low smoke generation characteristics since these two phenomena can be the result of competing mechanisms. Flame retardants can interfere with the efficacy of the combustion of volatile species and can cause sooty air-borne particles to be formed, while low smoking composites can create higher heats of combustion to more efficiency consume combustible organic gases.

Certain disclosures that are relevant to the present invention exist in the prior art concerning blending a

vinyl chloride resin with branched alkylene glycol bis(diphenyl phosphate) compositions. For example, British Patent No. 2,061,949 describes the addition of such bisphosphates at amounts of up to 10 parts by weight of bisphosphate per 100 parts by weight of vinyl chloride resin. Somewhat higher amounts of such bisphosphates (namely, up to about 20 wt% per 100 parts by weight of vinyl resin) are shown in Japanese Patent Publication No. 40342/74, but only in the presence of significantly higher amounts (30 wt% to 50 Wt%) of another, more conventional plasticizer (e.g., dioctyl phthalate). Finally, while U.S. Patent No. 3,869,526 to M. Combey et al. also described the use of these bisphosphates, it specifically excludes those that contain aryl substitution of six to eight carbon atoms on all four -OR substituents attached to the two phosphorus atoms. This excludes, for example, neopentyl glycol bis(diphenyl phosphate) compositions from selection for use in the Combey invention.

The present invention relates to the use of a neopentyl glycol bis(diphenyl phosphate) composition, as the major plasticizing additive, to function as a very effective flame retardant in PVC composites, when used in amounts that are no less that about 25 wt%, by weight of the PVC (for example, from about 35 wt% to about 125 wt%, as exemplified by use at from about 40 wt% to about 90 wt% by weight of the PVC) while also contributing significantly less smoke than does a representative triaryl monophosphate ester. The flexibility of the resulting composition that is imparted to vinyl compounds by use of the present invention is similar to that obtained by use of a triaryl phosphate plasticizer. While other plasticizing additives can be also present in the composition, they will be present in lower amount than the amount of neopentyl glycol bis(diphenyl phosphate) composition.

EXAMPLES

Vinyl Formulations

Components	1	2	3	4
S-PVC (K=71)	100	100	100	100
INTERLITE ZG6067/3	5	5	5	5
ESTABEX E2307	2	2	2	2
PHOSFLEX 390	60			
NPGDP		60	60	60
Zinc Borate			6	6
AOM LS030				6

The vinyl resin used was a suspension type PVC with a K value of 71. The INTERLITE brand stabilizer (from Akcros) was a mixture of metal soaps, antioxidants and acid scavengers and the ESTABEX 2307 brand product (also from Akcros) was a epoxy stabilizer. The phosphate esters used in this evaluation were: PHOSFLEX 390 brand (P-390) from Akzo Nobel Functional Chemicals LLC, an alkyl diphenyl phosphate commonly used in wire and cable applications as a flame retardant/plasticizer; and "NGPDP", which represents neopenytl glycol bis(diphenyl phosphate). Also included in this screening experiment were certain common flame retardant synergists and smoke suppressants, namely, zinc borate (from J. Storey) and ammonium octamolybdate (AOM LS030 brand).

The above formulations were compounded on a two-roll mill for a sufficient time to achieve homogeneity. The milled sheets were compression molded to specimen size to perform cone calorimeter analysis. The results are as follows:

Cone Calorimeter Study of Phosphate Esters in Vinyl Composites:

Composite No. :	1	2	3	4
Plasticizer	P-390	NPGDP	NPGDP	NPGDP
Zinc borate	-	-	6	6
AOM	-	-	-	6
Cone Data*				
Peak Heat Release Rate (PHRR)	261.36	205.86	165.21	158.32
Avg. Specific Extinction Area	1126.33	1135.85	1037.72	1039.69
Time To Ignition (TTI)	16.97	22.31	26.16	22.17
Fire Performance Index	0.065	0.108	0.158	0.140
Smoke Parameter	294	234	171	165
CO	0.133	0.160	0.125	0.111
CO_2	1.328	1.280	1.372	1.413

*Cone Calorimeter: 50kW/m^2 heat flux

Discussion of Composite Testing Results:

Compared with the control flame retardant plasticizer, PHOSFLEX 390 brand (Ccomposite No.1), the cone flammability data suggests that NPGDP (No.2), at equivalent levels, performs as well or better in low smoke generation (see the lower specific extinction area - "SEA") and has a significantly less peak heat release rate than isodecyl diphenyl phosphate. Both the heat release rate and smoke generation of neopentyl glycol bis(diphenyl phosphate)/vinyl composites were further improved with the addition of zinc borate (see Composite Nos.3 and 4). Converting this information into calculated values such as the "fire performance index" (the time to ignition divided by the peak heat release rate - a higher value implies greater fire performance) demonstrated significantly better performance than the use of neat P-390. Another calculated reference, the "smoke parameter" is derived from calculations of the peak heat release rate times the specific extinction area (smoke obscuration) divided by 1000 (lower value implies improved low smoke efficiency). The addition of the smoke suppressant ammonium

octamolybdate (No.4), showed a slight improvement to low smoke generation but is not considered to have a significant influence on the fire or smoke performance of the composite.

Although the use of neopentylene bis (diphenyl phosphate) as the sole FR additive showed low smoke and high flame retardant efficacy in vinyl composites, such characteristics can be further boosted in the presence of certain additional flame retardant additives. For example, the addition of zinc borate and ammonium octamolybdate have shown an exceptional boost in flame resistance and low smoke generation when blended with the aforenemtioned alkylene bridged bisphosphate (see Formulation Nos. 5 and 6, which are in accordance with the present invention, in the first Table set forth below). At fifty parts per hundred (phr) of plasticizer in a flexible vinyl formulation, a significant reduction of smoke generation was seen (about a twenty-eight percent decrease).

Similarly formulated composites using another monophosphate ester (i.e., the SANTICIZER 2148 brand product, an alkylated diphenyl phosphate, from Ferro) and certain non-FR plasticizer types (DINP, diisononyl phthalate, from Exxon and TOTM, trioctyl trimellitate, from Sunoco), although in some cases demonstrating low smoke values, do not match the low smoke performance seen with combinations of the inorganics with the alkylene-bridged bisphosphate NPGDP (see the second Table set forth below).

Formulation Nos.:	5	6	7	8	9	10
PVC (k value = 71)	100	100	100	100	100	100
CaCO3	10	10	10	10	10	10
Alumina Trihydrate (Hydral 710)	30	30	30	30	30	30
Zinc Borate		6	6	6	6	6
AOM		6	6	6	6	6
NPGDP	50	50				
TOTM						50
SANTICIZER 2148					50	
DINP			50			
PHOSFLEX 31L				50		
Epoxidized Soybean Oil (ESO)	5	5	5	5	5	5
Dibasic Lead Phthalate (DYTHAL)	5	5	5	5	5	5
BZ-4975	2.5	2.5	2.5	2.5	2.5	2.5
Totals:	202.5	214.5	214.5	214.5	214.5	214.5

Formulation Nos.:	5	6	7	8	9	10
Flammability	NPGDP	NPGDP/FRs	DINP	31L	S2148	TOTM
LOI:	33	34	28	37.5	29	27.5
1.6mm						
UL-94 (1.6mm)	V-0	V-0	FAIL	V-0	V-0	V-1
(AFT)	0	0	>4"	0.1	0.5	2.6

Cone Calorimeter Results	NPGDP	NPGDP/FRs	DINP	31L	S2148	TOTM
TTI	34.75	21.76	16.27	47.85	18.13	17.53
PHRR	172.63	130.23	253.92	151.52	261.89	229.83
Specific Extinction Area(Smoke)	806.17	582.15	791.75	958.24	809.44	715.02
Fire Protection Index	0.201	0.167	0.064	0.316	0.069	0.076
Smoke Parameter	139	76	201	145	212	164
Average CO_2	0.8332	1.0563	0.9633	0.8459	1.0343	0.9891
Average CO	0.1113	0.0575	0.0710	0.1089	0.0795	0.0795

The foregoing Examples have been presented to illustrate certain embodiments of the present invention and, for that reason should not be construed in a limiting sense. The scope of protection desired is set forth in the Claims that follow.

What is Claimed:

1. A vinyl chloride resin composition that comprises as the major plasticizer a neopentyl glycol bis(diphenyl phosphate) composition in an amount that is no less than about 25% by weight, based upon the vinyl chloride resin being present at 100%, by weight.

2. A composition as claimed in Claim 1 wherein the neopentyl glycol bis(diphenyl phosphate) composition is present at from about 35% to about 125%, by weight.

3. A composition as claimed in Claim 1 wherein the neopentyl glycol bis(diphenyl phosphate) composition is present at from about 40% to about 90%, by weight.

4. A composition as claimed in any one of Claims 1-3 wherein additional flame retardant and smoke suppressant synergists are present.

5. A composition as claimed in Claim 4 wherein zinc borate is additionally present.

6. A composition as claimed in Claim 4 wherein ammonium octamolybdate is additionally present.

INTERNATIONAL SEARCH REPORT

Inte[illegible]onal Application No
PCT/U[illegible]/20012

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/523 C08L27/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 976 616 A (COMBEY MALCOLM ET AL) 24 August 1976 (1976-08-24) claim 1	1-3
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 September 2003	24/09/2003

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Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte[illegible]nal Application No
PCT/[illegible]3/20012

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